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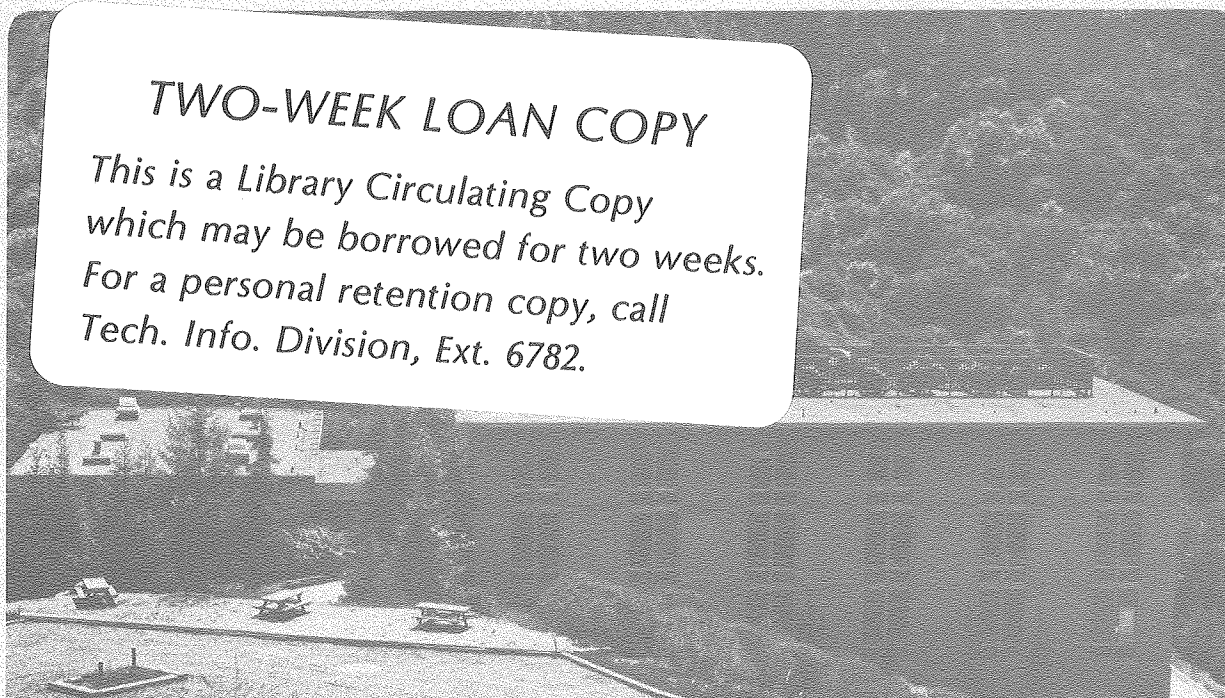LBL-11735 c.2

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THE PARABOLIC GROWTH OF OXIDE SOLID SOLUTIONS

ON BINARY ALLOYS: A SEMI-EMPIRICAL APPROACH

D.P. Whittle*, F. Gesmundo**, and F. Viani**

Abstract

The growth of solid solution oxide scales on alloys has been described by considering either the transport of the cations themselves, or that of the defect species in the oxide lattice. The two approaches have been shown to be similar. However, it has become apparent that the simplified defect model implicitly assumed in previous analyses using the ionic transport approach is not adequate to fully describe the variation of ionic diffusivities with oxygen potential or oxide composition. Further analyses, using a combination of the two approaches, are suggested.

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INTRODUCTION

The growth of solid solution scales containing ions of the same valence on binary monophase alloys has been examined by a number of authors [1-7], following the fundamental paper by Wagner [8]. Wagner's original equations described the simultaneous transport of two cations through a growing surface scale, and while these equations were quite general their application to a particular system requires a knowledge of the dependence of the self-diffusion coefficients of the two cations on both oxygen activity and oxide composition. Thus, a detailed knowledge, or model, of the defect structure of the oxide solution is required. Indeed, an alternative approach can be adopted that considers the transport of the defect species through the scale rather than the diffusion of the ionic species, as has been used for the growth of oxide scales on pure metals or oxide solutions containing ions of different valency [9].

This paper, then, will show that the two approaches are similar, although it will be demonstrated that consideration of lattice defect motion alone is not sufficient for the case of growth of an oxide solution, since in these terms the two types of cations are essentially identical. A following paper [10] will demonstrate that using a more complete model for the oxide defect structure allows a more complete treatment of the growth of solid solution scales to be presented.

THEORY

Thermodynamics of Defects in an (AB)O Solid Solution

The variation in concentration of lattice defects with composition in a solid solution oxide containing two kinds of metallic cations of the same valency has been analyzed by a number of workers, of which the more relevant are Zintl [11], Chen and Peterson [12], and Dieckmann and Schmalzried [13]. However, for the most part these treatments have primarily been directed at interpretations of the variation of experimentally determined phenomenological variables, such as ionic diffusion coefficients or electrical conductivities, as functions of the equilibrium parameters of the system. The models used to interpret the behavior have generally been formulated on the basis of a simple approximation that only one kind of defect, usually a cation vacancy, prevails. This approach may well be adequate when the oxygen potential range considered is not very great; however, it is becoming increasingly clear (see, for example, Kofstad [14]), from measurements of electrical conductivity and of tracer and chemical diffusion coefficients over wide ranges of oxygen potential, that this simple approximation is no longer adequate and that a more complete model for the defect structure of the oxide is necessary. This is especially true for the interpretion of the parabolic growth rate of a pure oxide on a pure metal [9], since the oxygen potential varies from the dissociation pressure of the oxide at the inner

oxide/metal interface to the ambient oxygen pressure, usually 1 atm. at the outer oxide surface. The same kind of considerations apply to the growth of solid solution scales, requiring as complete a description as possible of the defect structure of the oxide solution and hence the variation of its transport properties with composition and oxygen potential.

Consider, then, the oxide solid solution formed from component oxides AO and BO, which have the same crystal structure. Typical oxides falling within this category include FeO, CoO, NiO, MnO, and MgO, all of which have the B1 rock-salt structure, and within certain temperature and oxygen potential ranges form complete solid solutions, (AB)O. Here it is assumed that the BO-compound is the more stable oxide. In what follows it will be assumed that the defect structures of the pure component oxides are known, that electron transport is much more rapid than ionic transport (semiconducting oxides), and that the presence of defects in the oxygen sublattice and interstitial cations can be neglected. In addition, it will be assumed that interactions between the different types of defects can be ignored. All these assumptions are generally acceptable to workers in this field, and there are no experimental data to the contrary.

The quasi-chemical equations for the formation of cation vacancies in a pure oxide, AO or BO, may be written in the general form

$$1/2 \ O_2 \ = \ O^X + V^X \tag{1a}$$

$$V^X \ = \ V' + h^{\bullet} \tag{1b}$$

$$V' \ = \ V'' + h^{\bullet} \tag{1c}$$

where the Kroger–Vink notation has been used, and will be used throughout. These equations give rise to corresponding equilibrium constants, which are indicated by $K_{V^X}^{AO}$, $K_{V'}^{AO}$. and $K_{V''}^{AO}$, respectively, for Eqs. (1a) through (1c) for pure AO, and $K_{V^X}^{BO}$, $K_{V'}^{BO}$, and $K_{V''}^{BO}$ for pure oxide BO. These equilibrium constants are of course related to the standard free energies of formation of the various defects in the two pure oxides: $(\Delta G_{V^X}^{o})^{AO}$, $(\Delta G_{V'}^{o})^{AO}$, $(\Delta G_{V''}^{o})^{AO}$, and $(\Delta G_{V^X}^{o})^{BO}$, $(\Delta G_{V'}^{o})^{BO}$, $(\Delta G_{V''}^{o})^{BO}$, respectively.

In the solid solutions, (AB)O, the free energies of formation of each kind of defect is expected to be different from those of the pure oxides and to be a function of the solid solution composition. As indicated earlier, when the component oxides AO and BO are of the same crystal type and form a complete homogeneous solid solution over their entire composition range, the resulting solution often approximates to thermodynamically ideal behavior. This is indeed the case for many of the cubic oxide solutions referred to earlier (see, for example, NiO–CoO [15]).

As a consequence, it seems appropriate to approximate the free energy of formation of a defect i (i = V^X, V', or V") in the

solid solution oxide ΔG_i^0 to a composition weighted average.
Thus

$$\Delta G_i^0 = (1 - \xi)(\Delta G_i^0)^{AO} + \xi(\Delta G_i^0)^{BO},$$
$$i = V^X, \ V', \ V'' \qquad (2)$$

ξ is the mole fraction of oxide BO (the more stable component) in
the oxide solution. It should be noted for later reference that ξ
is also the equivalent fraction of component BO in the solid
solution, since the valencies of the two cations z_A and z_B are
identical, and equal to $|z_0|$. It should also be noted that
Eq. (2) is consistent with the transport coefficients of cations A
and B, varying proportionally to the exponential of the oxide
composition at a fixed oxygen potential (a single kind of defect
prevailing): a relationship verified experimentally for these
transition metal oxides [16]. Using the general relationship
between free energy change and equilibrium constant, and putting

$$\Delta G_i^0 = -RT \ \ln \overline{K}_i, \qquad i = V^X, \ V', \ V'' \qquad (3)$$

where $\overline{K}_i$ represents the quasi-equilibrium constant for the
formation of vacancies of type i in the oxide solution, a
combination of Eqs. (2) and (3) then gives

$$\overline{K}_i = K_i^{AO}(K_i^{BO}/K_i^{AO})^{\xi}, \quad i = V^X, V', V'' \tag{4}$$

Thus, with reference to the reactions described in Eq. (1)

$$\overline{K}_{V^X} = [V^X]/a_0, \qquad K_{V'} = [V']p/[V^X],$$

$$\overline{K}_{V''} = [V'']p/[V'] \tag{5}$$

where [ ] denote concentration (Henry's law assumed) and p replaces $[h^{\bullet}]$. The composition dependence of the various defect concentrations are then given by

$$[V^X] = \overline{K}_{V^X} a_0 = K_{V^X}^{AO}(K_{V^X}^{BO}/K_{V^X}^{AO})^{\xi} a_0 \tag{6a}$$

$$[V'] = \overline{K}_{V'}[V^X]/p = K_{V^X}^{AO}K_{V'}^{AO}(K_{V^X}^{BO}K_{V'}^{BO}/K_{V^X}^{AO}K_{V'}^{AO})^{\xi}(a_0/p) \tag{6b}$$

$$[V''] = \overline{K}_{V''}[V']/p = K_{V^X}^{AO}K_{V'}^{AO}K_{V''}^{AO}(K_{V^X}^{BO}K_{V'}^{BO}K_{V''}^{BO}/K_{V^X}^{AO}K_{V'}^{AO}K_{V''}^{AO})^{\xi}(a_0/p^2) \tag{6c}$$

In order to calculate the concentrations of all the defects, as functions of oxygen potential and solid solution composition, the local neutrality condition must be established in addition to knowing the various constants in Eq. (6). The formation of

electronic defects in these oxides may be represented by the quasi-chemical equation null $= e' + h^{\bullet}$, which has an equilibrium constant, K_{el}, given by

$$K_{el} = p \cdot n \tag{6d}$$

where n replaces $[e']$. Thus, the electroneutrality condition becomes

$$p = [V'] + 2[V''] + n \tag{7}$$

Substitution of Eq. (6) in Eq. (7) gives a cubic equation relating p with ξ and a_0:

$$p^3 - K_{V^x}^{AO} K_{V}^{AO} (K_{V^x}^{BO} K_{V}^{BO} / K_{V^x}^{AO} K_{V}^{AO})^{\xi} a_0 p - K_{el} p$$

$$- 2\, K_{V^x}^{AO} K_{V}^{AO} K_{V}^{AO} (K_{V^x}^{BO} K_{V}^{BO} K_{V}^{BO} / K_{V^x}^{AO} K_{V}^{AO} K_{V}^{AO})^{\xi} = 0 \tag{8}$$

When Eq. (8) is solved, the concentrations $[V']$ and $[V'']$ can be obtained from Eqs. (6b) and (6c), respectively; the concentration $[V^X]$ is independent of the charge balance and is obtained directly from Eq. (6a), while n is obtained from Eq. (6d).

Transport Equations

General transport equations for the parabolic growth of an oxide on either a pure metal or dilute alloys forming an oxide doped with an aliovalent cation with a uniform or nonuniform distribution of the dopant have been developed [9] that take into account the real complexities of the oxide defect structure. In essence, the fundamental equation expressing the overall flux of defects (vacancies) J_{def} in the growing oxide is given by

$$J_{def} = \Omega \{ D_{V^X}[V^X] + D_{V^{'}}[V^X] + D_{V^{''}}[V^{''}] \} \, d \ln a_0 / dx$$

$$(9)$$

where x is distance in the scale measured from the alloy/scale interface, Ω is a proportionality factor required to convert the concentrations of defects, usually expressed as mole fractions to the more convenient units of numbers of defects/unit volume: Ω equals $N_A \rho_{ox}/M_{ox}$ (N_A being Avogadro's number, ρ_{ox} the oxide density, and M_{ox} its molar weight). The D_i's and $[i]$'s are the transport coefficients and concentrations of the species indicated. Multiplying through Eq. (8) by dx, integrating from x=0 to $x=x_s$ where x_s is the instantaneous scale thickness, and recalling that to a very good approximation, J_{def} is constant with respect to x for a given x_s, yields

$$J_{def} \cdot x_s = K_t = \Omega \int_{a_0'}^{a_0''} \Sigma (D_{def}[def]) \cdot d \ln a_0 \tag{10}$$

where a_0' and a_0'' are the oxygen activities at the alloy/scale and scale/gas interfaces, respectively, and $\Sigma (D_{def}[def])$ has replaced the expression in chain brackets in Eq. (9). K_t is the parabolic rate constant for scale growth expressed as molecules of oxide formed per unit surface area per unit time for unit scale thickness (molecules/cm^2/s) and may be converted into the more common constant, K_x, expressed in terms of overall scale thickness by

$$x_s^2 = K_x t \tag{11}$$

using the relationship

$$K_x = 2 K_t / \Omega \tag{12}$$

If Eq. (9) is again multiplied through by dx and integrated from $x = 0$ to a given value of $x \leq x_s$, then

$$J_{def} \cdot x = \Omega \int_{a_0'}^{a_0} \Sigma (D_{def}[def]) \, d \ln a_0 \tag{13}$$

Dividing Eq. (13) by Eq. (10), using Eq. (12) gives

$$x/x_s = y = 2/K_x \int_{a_0'}^{a_0} \Sigma (D_{def}[def]) \, d \ln a_0 \tag{14}$$

giving the profile of a_0 as a function of the dimensionless

position, y, through the scale.

In order to evaluate the integral in Eq. (14), and hence

calculate the oxygen activity profile through the scale and the

parabolic rate constant K_x, the function $\Sigma(D_{def}[def])$ must be

known. For a pure oxide, this is straightforward [9] since

$\Sigma(D_{def}[def])$ is only a function of a_0 and is obtained through

the simultaneous solution of Eqs. (8) and (6) with $\xi = 0$ or 1 (pure

oxide). In the present case in which the oxide contains two types

of metallic cation, this is not possible: $\Sigma(D_{def}[def])$ depends

on both a_0 and ξ, and as a consequence the dependence of ξ on

the local position in the scale (or on a_0, although ξ is not a

single-valued function of a_0) is also required. The variation of

ξ through the scale cannot be obtained from the present analysis in

its current form. Only the motion of lattice defects has been

considered, and in these terms the two types of cations are

considered essentially identical. However, as will be discussed

later, differences in the rates of exchange of the different cations

with neighboring defects (jump frequencies) and correlation effects

give rise to the cation concentration profiles that develop in the

growing scale.

One approach to overcome this dilemma is to use

experimentally determined cation concentration profiles, i.e.,

$\xi = f(y)$, as input data so that the calculations can then be

completed. Gesmundo and Viani [9] have carried out such

calculations for assumed cation distributions in oxide scales consisting of a noble metal oxide doped with a small concentration of an aliovalent cation. Here, interest is in oxide solutions containing cations of the same valency, and in the following section similar types of calculation are carried out for the oxidation of Ni-Co alloys using the experimentally measured concentration profiles [6].

ANALYSIS OF Ni-Co ALLOY OXIDATION

The measured concentrations [6] through the scales formed on four Ni-Co alloys oxidized at $1000°C$ in 1 atm. oxygen are shown in Fig. 1. Different samples had been oxidized for different periods of time, but all the concentration profiles have been reduced to the same dimensionless scale , $y = x/x_s$. An analytical expression has been fitted to the various profiles to give $\xi(y)$, and these are included as the solid lines in Fig. 1.

In addition, the values of the equilibrium constants for the formation of the different ionic and electronic defects in the two pure oxides, NiO and CoO, are required. For CoO, these have been measured by a number of authors and are summarized by Dieckmann [17]. At $1000°C$,

$$K_{V^X}^{CoO} = 1.37 \times 10^{-3}, \ K_{V'}^{CoO} = 1.94 \times 10^{-2},$$

$$K_{V^X}^{CoO} = 1.89 \times 10^{-4}, \text{ and } K_{el} = 10^{-9}.$$

As indicated earlier, the presence of interstitial defects has been neglected. Corresponding values for pure NiO [18] are:

$$K_{V^X}^{NiO} = 5.20 \times 10^{-6}; \quad K_{V'}NiO = 2.92 \times 10^{-3};$$

$$K_{V''}^{NiO} = 5.33 \times 10^{-5}; \quad K_{el} = 1.12 \times 10^{-16}.$$

The diffusion coefficient of the vacancies is assumed to be independent of their charge, and also independent of oxide composition, although the latter assumption is not strictly valid [13], and this will be discussed in a later paper.

In the present analysis, the value for CoO at 1000°C has been used as reported by Dieckmann [17]:

$$D_{def} = 2.975 \times 10^{-7} \ cm^2/s.$$

In order to then solve Eq. (14) using Eqs. (8) and (6), the function $\xi(y)$, and the data above, an iterative procedure is necessary. A tentative profile, $a_0(y)$, is assumed (zero-order approximation) and this is used to evaluate the corresponding concentration profiles of all the defects, the parabolic rate constant, K_x, and a new profile $a_0(y)$ (first-order approximation). The entire calculation is then repeated using this new $a_0(y)$ profile, and the process is repeated until successive iterations of K_x differ by less than a prescribed amount. A

convenient profile of $a_0(y)$ to initiate the calculation is that for a uniform distribution of cobalt in the oxide, with a concentration equal to that of the bulk alloy.

Figures 2a, 2b, 2c, and 2d show the variations of [V"], [V'], [V^X], p, and n across the scale formed on Ni - 10.9 percent, 20 percent, 38 percent, and 80 percent Co, respectively, at 1000°C. As indicated earlier, these have been calculated using the experimentally measured Co distributions through the oxide. A number of points emerge from these calculations:

(a) singly charged vacancies, V', predominate, expecially at higher oxygen potentials for all the alloys,

(b) as the cobalt content of the alloy and hence the Co concentration in the oxide increases, the concentrations of V^X and e' become increasingly significant,

(c) and as the cobalt content of the oxide increases, the total concentration of all types of defect increases.

These calculations also give the oxygen potential variation across the oxide and the parabolic growth rate of the scale. These latter values are shown in Fig. 3 (dashed curve) and are compared with the available experimental data. It should be noted, as pointed out earlier, that the calculations have been carried out assuming that D_V is independent of composition, and the value of D_V in pure CoO has been used (2.975×10^{-7} cm^2/s). However, measurements of D_V in pure NiO give a value of 1.31×10^{-7} cm^2/s at 1000°C. Thus, the calculated values of the rate constant are somewhat

sensitive to the value of D_V used, although the defect
concentration profiles are not. The full curve in Fig. 3 has been
recalculated taking into account that D_V varies linearly with
composition, although this too is somewhat of an
approximation (13). Thus, the agreement between calculated and
experimental rate constants in Fig. 3 is quite acceptable.

PREDOMINANCE OF A SINGLE TYPE OF DEFECT

The previous treatment requires that all the equilibrium
constants (or free energies of formation) for all the kinds of
vacancies and for the intrinsic ionization for both pure oxides are
known with a sufficient accuracy. Since this is not generally the
case, some simplification is often necessary. This is achieved by
assuming that only one kind of vacancy predominates in the oxide
solution over the entire range of oxygen potential involved in the
growth of the oxide. It is also convenient to assume that
negatively charged electronic defects can be ignored. Under these
assumptions, the pseudo-chemical equation for the formation of a
vacancy of charge z is

$$1/2 \ O_2 = O^X + V^{z'} + zh^{\bullet} \tag{15}$$

and the corresponding equilibrium constants for the two pure oxides
are given as $k_V^{AO}z'$ and $k_V^{BO}z'$, respectively. It should be
noted that these equilibrium constants, denoted by lower case k's

are slightly different in form than those referring to Eq. (1) given

earlier. Since only one kind of defect predominates, the equation

for its formation is written relative to the perfect lattice, and it

is thus easy to show that when $z = 1$, for example,

$k_{V'}^{AO} = K_{V^x}^{AO} k_{V'}^{AO}$. Using a procedure similar to

before in considering the free energy of formation of defects in the

oxide solution as a linear function of its composition gives

$$k_{V^{z'}} = k_{V^{z'}}^{AO} \; (k_{V^{z'}}^{BO}/k_{V^{z'}}^{AO})^{\xi} \tag{16}$$

and

$$k_{V^{z'}} = [V^{z'}] p^z / a_0 \tag{17}$$

The three values of $z = 0$, 1, and 2 are considered below.

(a) Neutral vacancies: $z = 0$

$$\bar{k}_{V^x} = [V^x]/a_0 = k_{V^x}^{AO}(k_{V^x}^{BO}/k_{V^x}^{AO})^{\xi} \tag{18a}$$

giving

$$[V^x] = k_{V^x}^{AO} \; (k_{V^x}^{BO}/k_{V^x}^{AO})^{\xi} \; a_0 \tag{20A}$$

(b) Singly charged vacancies: $z = 1$

$$\bar{k}_{V'} = [V'] p/a_0 = k_{V'}^{AO} \; (k_{V'}^{BO}/k_{V'}^{AO})^{\xi} \tag{18b}$$

giving

$$[V'] = k_V^{AO}(k_V^{BO}/k_V^{AO})^{\xi}\, a_0/p \tag{19b}$$

Using the electroneutrality condition, Eq. (7), which for this case is $p = [V']$, yields

$$[V'] = \quad k_V^{AO}(k_V^{BO}/k_V^{AO})^{\xi}\; 1/2\; a_0^{1/2} \tag{20b}$$

(c) Doubly charged vacancies: $z = 2$

$$\bar{k}_{V''} = [V'']p^2/a_0 = k_{V''}^{AO}(k_{V''}^{BO}/k_{V''}^{AO})^{\xi} \tag{18c}$$

giving

$$[V''] = k_{V''}^{AO} (k_{V''}^{BO}/k_{V''}^{AO})^{\xi}\; a_0/p^2 \tag{19c}$$

In this case, the electroneutrality condition is $p = 2[V'']$, and thus

$$[V''] = (1/4)^{1/3}\; \{K_{V''}^{AO}(K_{V''}^{BO}/K_{V''}^{AO})^{\xi}\}\; 1/3\, a_0^{1/3} \tag{20c}$$

Equation (20) then gives the defect concentration, assuming that only a single type of defect predominates. However, although these expressions are somewhat simpler than those for the more general case given earlier, [def] is still a function of both oxygen potential, a_0, and oxide composition, ξ, and thus the function $\xi(y)$ is required before any solution can be obtained.   As an

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alternative to using experimentally determined profiles, as used
earlier, profiles could be calculated using the general transport
equations developed by Wagner [8] which consider the diffusion of
cations themselves rather than the defects. This is considered in
the next section.

Growth of the Scale Equations Using Ionic Transport

According to Wagner, the relationship between the rate
constant for growth of an oxide solution on a binary alloy and the
distribution of metal cation concentration and oxygen activity in
the scale is given by the following two interrelated equations:

$$D_A(1-\xi)[-\frac{\partial \ln a_{AO}}{\partial \xi} \frac{d\xi}{dy} + \frac{z_A}{z_0} \frac{\ln a_0}{dy}]$$

$$+ D_B \xi [- \frac{\partial \ln a_{BO}}{\partial \xi} \frac{d\xi}{dy} + \frac{z_B}{z_0} \frac{d\ln a_0}{dy} = K_x \tag{21}$$

$$yK_x \frac{d\xi}{dy} = - \frac{d}{dy} [D_B \xi (\frac{\partial \ln a_{BO}}{d\xi} \frac{d\xi}{dy} - \frac{z_B}{z_0} \frac{d\ln a_0}{dy})] \tag{22}$$

D_A and D_B are self-diffusivities of metal cations A and B,
respectively, in the oxide solution; the other parameters have been
defined earlier. For the case where $z_A = z_B = z_0$ and the
oxide solution is thermodynamically ideal, as discussed earlier,

Eqs. (21) and (22) reduce to

$$(D_A - D_B) \frac{d\xi}{dy} + [D_A(1-\xi) + D_B \xi] \frac{d\ln a_0}{dy} = K_x$$

(23)

and

$$yK_x \frac{d\xi}{dy} = -\frac{d\xi}{dy}[D_B(\frac{d}{dy} - \xi \frac{d\ln a_0}{dy})]$$

(24)

Bastow et al. [6] have solved these equations for the growth of
(NiCo)O on Ni-Co alloys, with good agreement between calculated and
experimental profiles. The solution requires a number of boundary
conditions that will not be detailed here. In addition, an
expression for the variation of the self-diffusivities of Ni and Co
ions with oxygen potential and oxide composition is required. These
were given by

$$D_A/D_B = P, \qquad D_B = D_B^0 \beta^{\xi-1} a_0^{1/\nu}$$

(25)

Here, P is used instead of p of the original equations to avoid
confusion with $p = [h^\bullet]$ defined earlier; P is a constant and is
essentially the ratio of the jump frequencies of the two cations,
β is the ratio of the concentration of cation defects (vacancies) in
pure BO to that in pure AO at unit oxygen activity, and ν depends on
the charge of the vacancies. These expressions, Eq. (25), have been
used by others in similar calculations [1-3, 6, 7, 20, 21].

Equation (25) is consistent with the analysis given earlier, provided that only one type of defect predominates. In fact, for vacancies $V^{z'}$, Eq. (20c) can be written in the general form

$$[V^{z'}] = [V^{z'}]_{BO}^{0} \ \beta^{-1} \ a_{0}^{1/v} \qquad (26)$$

where

$$\beta = (k_{V^{z'}}^{BO}, \ k_{V^{z'}}^{AO})^{1/3}, \qquad v = z + 1 \qquad (27)$$

Furthermore, assuming that the vacancy diffusion coefficient $D_{V^{z'}}$ is independent of composition (an assumption not strictly valid, as discussed earlier) but adopted here to be consistent with the earlier analysis, and using the usual relationship that

$$D_{B}^{0} = D_{def} \ [V^{z'}]_{BO}^{0} \qquad (28)$$

which is also an approximation for oxide solutions, as will be shown in a later paper [10], then Eqs. (26), (27), and (28) are consistent with Eq. (25).

COMPARISON OF THE TWO APPROACHES

In calculating the cation concentration, (y), and oxygen activity profiles, $a_0(y)$, through the scales formed on Ni-Co alloys oxidized in 1 atm oxygen at $1000°C$, Bastow et al. [6] used

the following values, which represented suitable values of the then available data:

$$P = 0.2, \quad \beta = 125, \quad v = 2.5, \quad D_{Co}^0 = 2.4 \times 10^{-9} \text{ cm}^2/s.$$

The use of a nonintegral value for v makes comparison with the present analysis difficult. Bastow et al. [6], however, show that values of v of 2 or 3 make little difference to the (y) profile. However, they do not report the $a_0(y)$ profiles. These have been recalculated and are shown in Fig. 4 along with the cobalt concentration profiles for an alloy containing 10.9 at. percent Co.

Using Eq. (26) it is now possible to examine how [V"] or [V'] (v = 3 or 2) varies through the scale according to this model, provided that $[V"]_{CoO}^0$ is known. At this point, only D_{Co}^0 has been used, which according to Eq. (28) is related to $D_{V"}$ (or $D_{V'}$) by

$$D_{Co}^0 = D_{V"}[V"]_{CoO}^0 = D_{V'}[V']_{CoO}^0 \tag{29}$$

Thus, for internal consistency, with the value of $D_{V"} = D_{V'} = 2.975 \times 10^{-7} \text{ cm}^2/s$ and $D_{Co}^0 = 2.4 \times 10^{-9} \text{ cm}^2/s$ at $1000°C$, this gives

$$[V"]_{CoO}^0 = 8.067 \times 10^{-3} \quad \text{or} \quad [V']_{CoO}^0 = 8.067 \times 10^{-3}.$$

Figure 5, then, shows the calculated variation of $[V'']$ ($v=3$) and $[V']$ ($v=2$) through the scale, and compares this with the values calculated using the equations given in the earlier section relating to the defect transport. These have been solved using the calculated $\xi(y)$ given in Fig. 4, the values of the equilibrium constants that are consistent with $[V'']^0_{CoO}$ and $[V']^0_{CoO}$ as given above, and $\beta = 125$, that is

$$v = 2 \quad k^{AO}_{V'} = 4.165 \times 10^{-9}, \quad k^{BO}_{V'} = 6.508 \times 10^{-5}$$

$$v = 3 \quad k^{AO}_{V'} = 1.075 \times 10^{-12}, \quad k^{BO}_{V''} = 2.100 \times 10^{-6}$$

Agreement between the two approaches is excellent. Indeed, the defect concentration profiles are really independent of the charge assumed on the defect, providing only a single charged species is considered, and of the approach used. The rate constants are also very similar. Using the ionic transport equations, these have values of $1.64 \times 10^{-10} cm^2/s$ and $2.13 \times 10^{-10} cm^2/s$ when only either V' or V'' are considered, respectively. They are moreover similar to the values obtained using the defect transport equations, 1.28×10^{-10} and $1.81 \times 10^{-10} cm^2/s$, respectively, under the same assumption regarding the defect nature of the oxide. These should be compared to $2.75 \times 10^{-10} cm^2/s$ given in Fig. 3 for this alloy and calculated using the defect transport approach with the experimentally measured Co concentration profiles and a complete

model for the defects, and $(0.4-1) \times 10^{-10} cm^2/s$ as reported [6] for experimentally determined values.

Of course the assumption of a single type of defect is an oversimplification, and Fig. 6 compares the defect concentration profiles calculated using this simplification (only V") with the results using the more realistic model for this alloy and given earlier in Fig. 2. An exact comparison is not very easy since different equilibrium constants for the defect equilibria have been used in the two calculations. However, it does indicate that a better description of the defect model to account for variation of the cation diffusion coefficients in the oxide solid solution ought to be incorporated in any analysis of the concentration profiles. This will be attempted in a following paper.

CONCLUDING REMARKS

The transport of ionic species across the parabolically growing oxide solid solution formed on an alloy can be described either by considering the diffusion of the cations themselves or of the defect species in the oxide lattice. The two approaches have been shown to be similar. However, the latter approach requires a priori knowledge of the distributions of the two cations, since consideration of the defects alone does not differentiate between the individual ionic species. However, it has become clear that the simplified defect model implicitly assumed in previous analyses using the ionic transport approach is not adequate to fully describe

the variation of ionic diffusivities with oxygen potential and oxide composition. Further analyses should use a combination of the two approaches.

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FIGURE CAPTIONS

Figure 1.   Measured concentration profiles through the scales
            formed on Ni-Co alloys oxidized at 1000°C (Ref. 22).

Figure 2.   Calculated concentrations of various defects across the
            NiO scale formed on (a) Ni-10.9 percent Co,
            (b) Ni-10 percent Co, (c) Ni-38 percent Co, and
            (d) Ni-80 percent Co oxidized at 1000°C (calculations
            based on the experimentally determined oxide
            compositions shown in Fig. 1).

Figure 3.   Calculated parabolic rate constants using the complete
            defect model approach as a function of composition.
            (Dashed curve is for D_V independent of composition.)
            Experimental values are also included.

Figure 4.   Calculated concentration profiles and oxygen activity
            profiles across the scale formed on Ni-10.9 percent Co
            at 1000°C using the ionic transport approach (Ref. 22)
            and a single defect model for the oxide solution.

Figure 5.   A comparison of the calculated variation of defect
            concentrations across the scale formed on
            Ni-10.9 percent Co oxidized at 1000°C using defect
            diffusion and ionic diffusion equations.

Figure 6.   A comparison of the calculated variation of defect
            concentrations across the scale formed on
            Ni-10.9 percent Co oxidized at 1000°C using a single
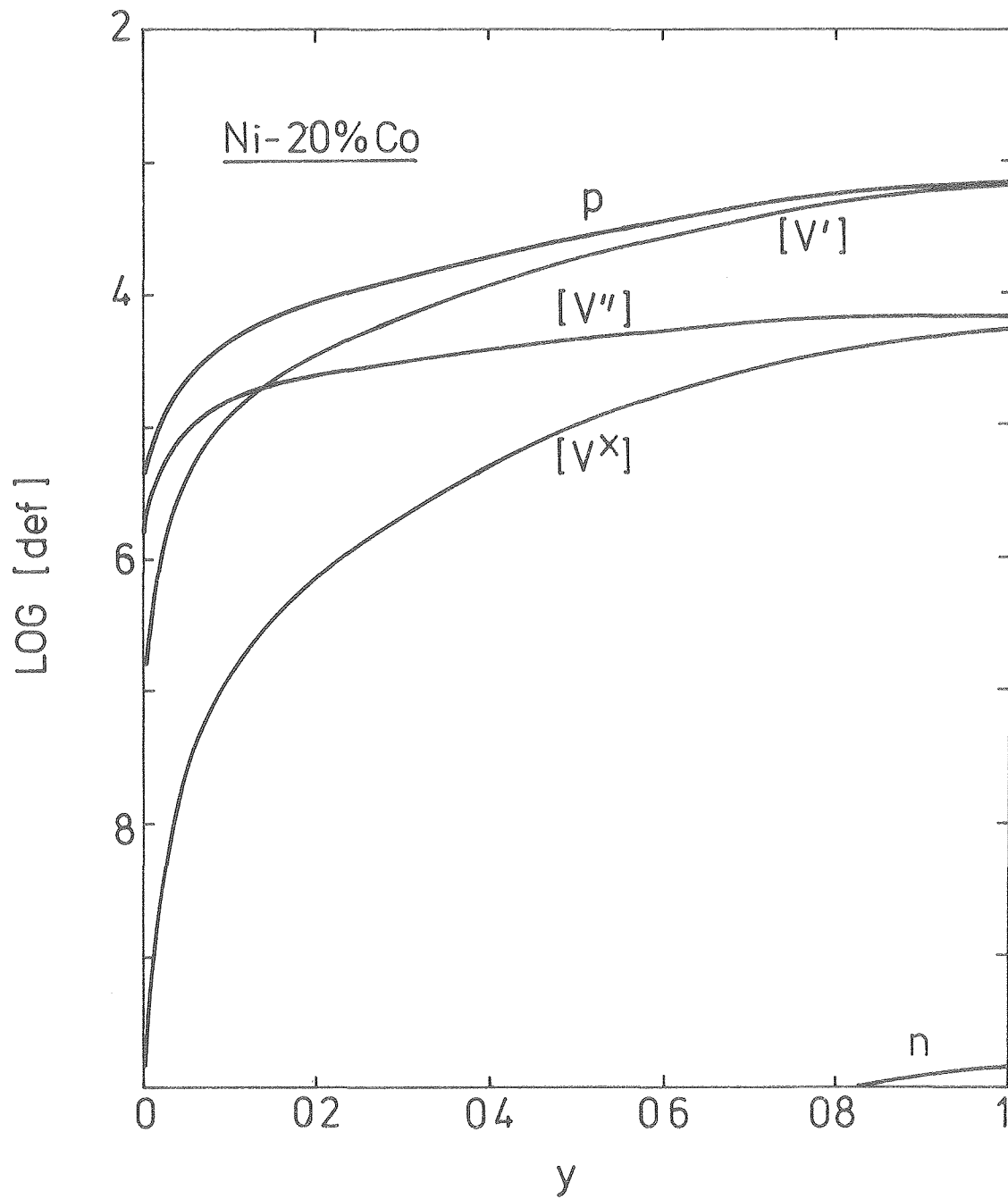   defect and a complete defect structure model.
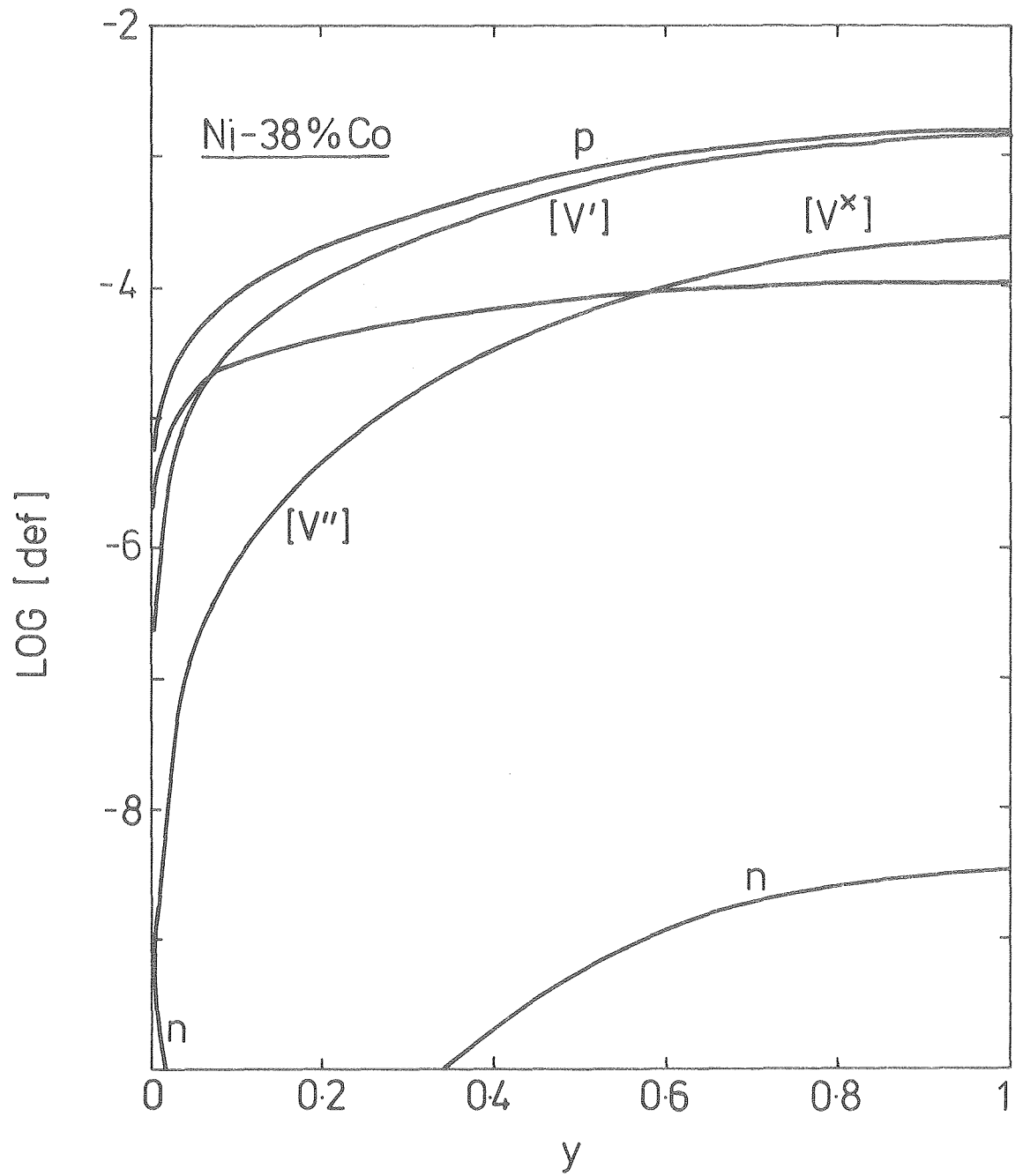
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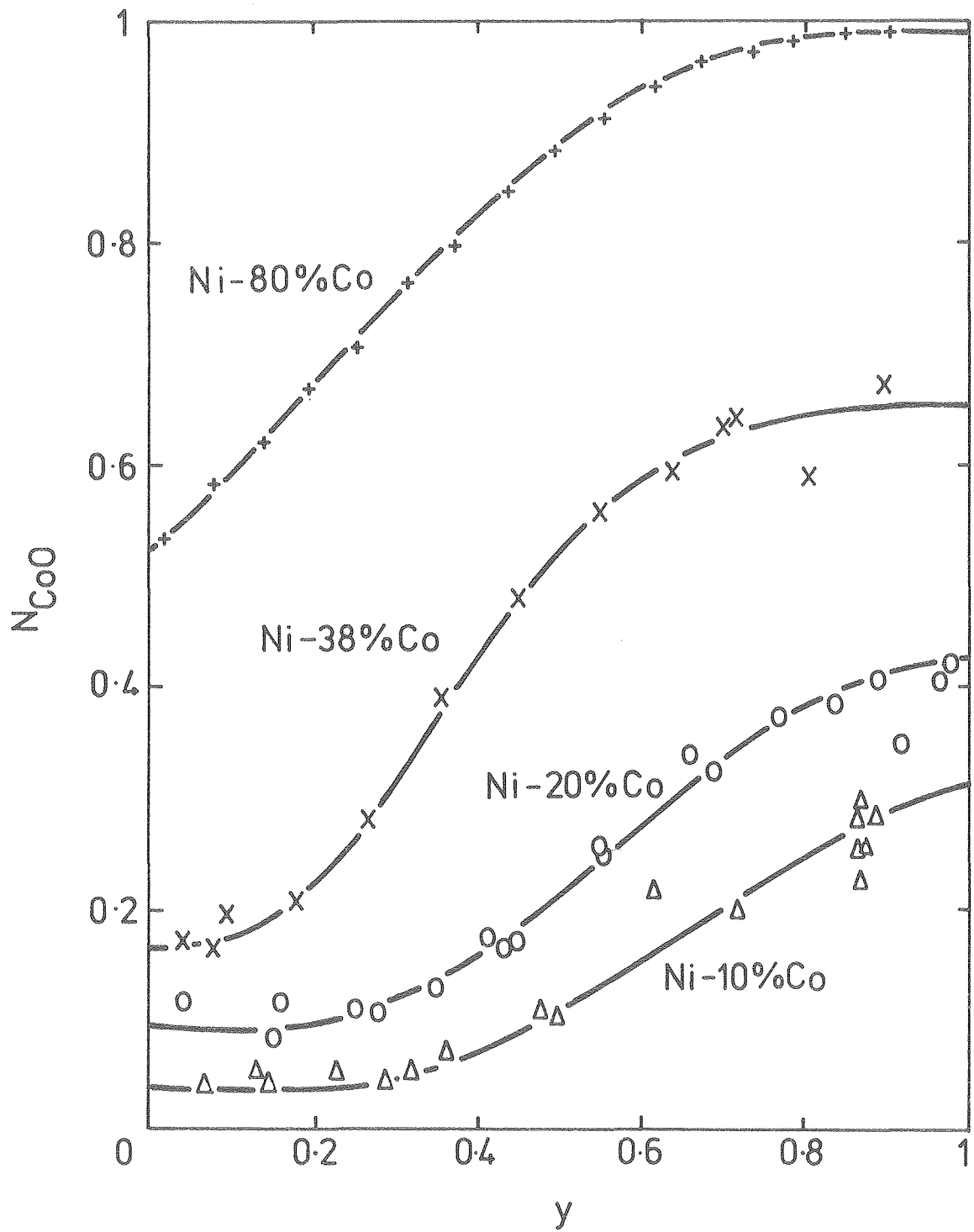
Figure 1

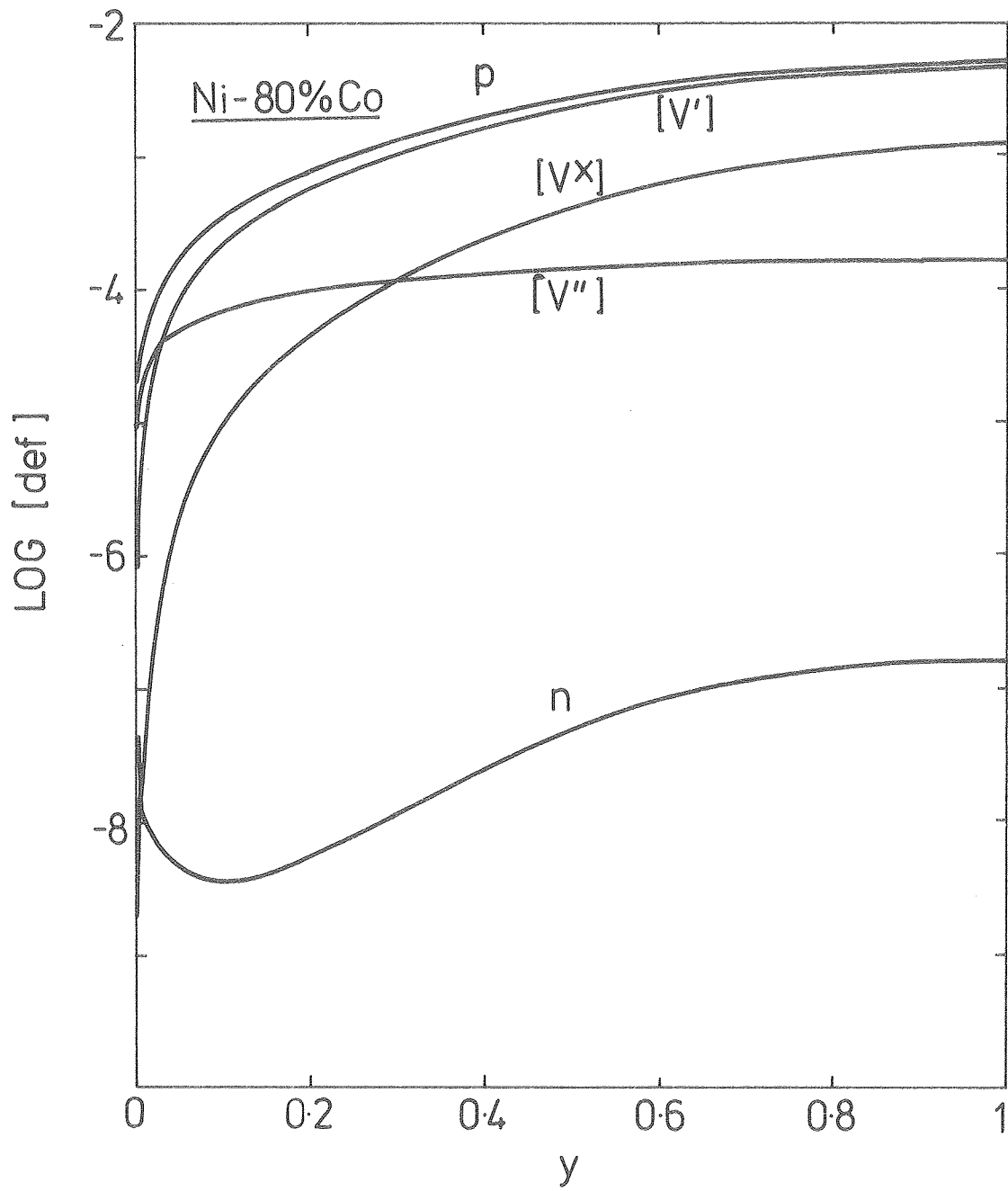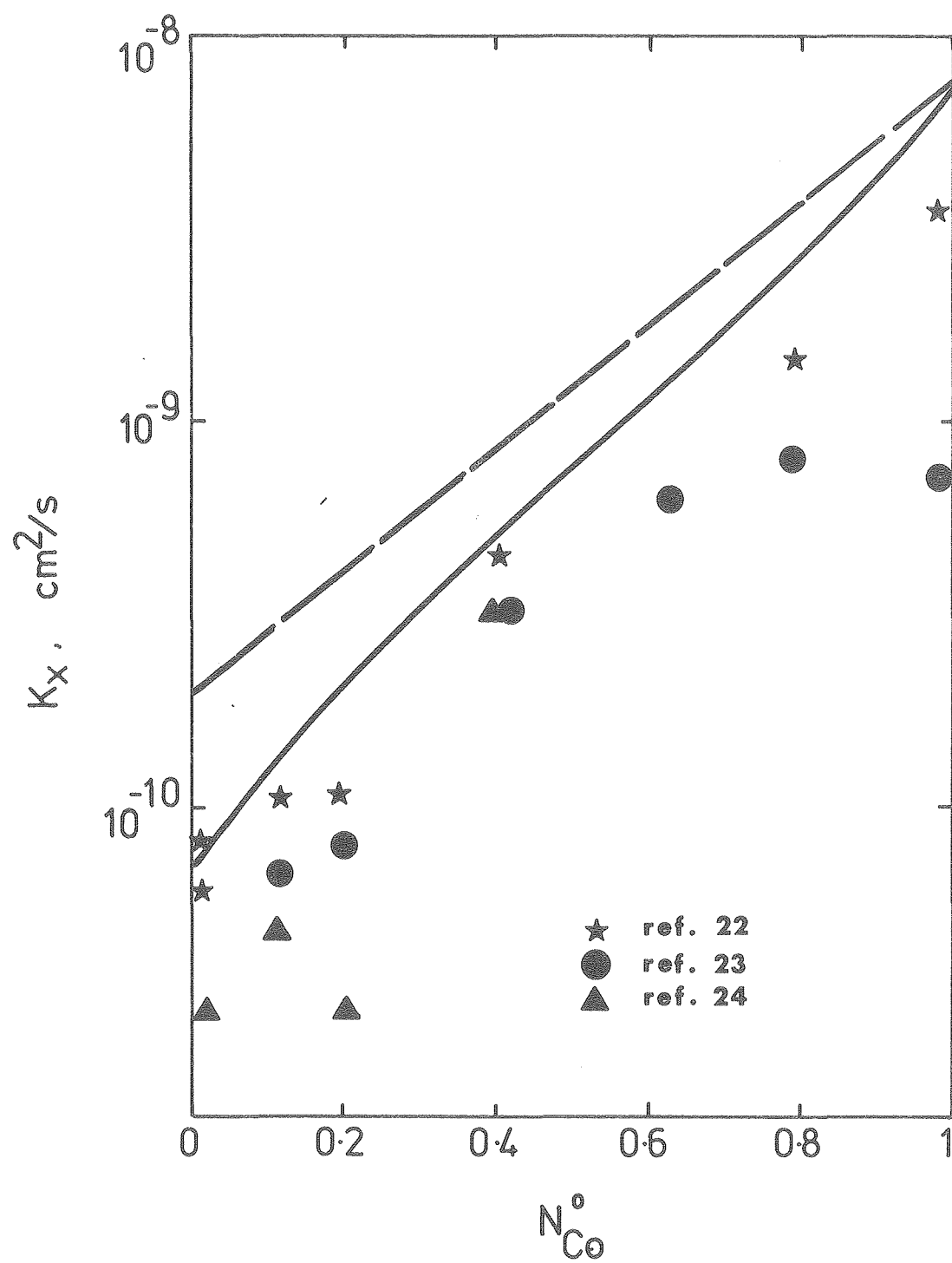XBL 809-11695

Figure 2a
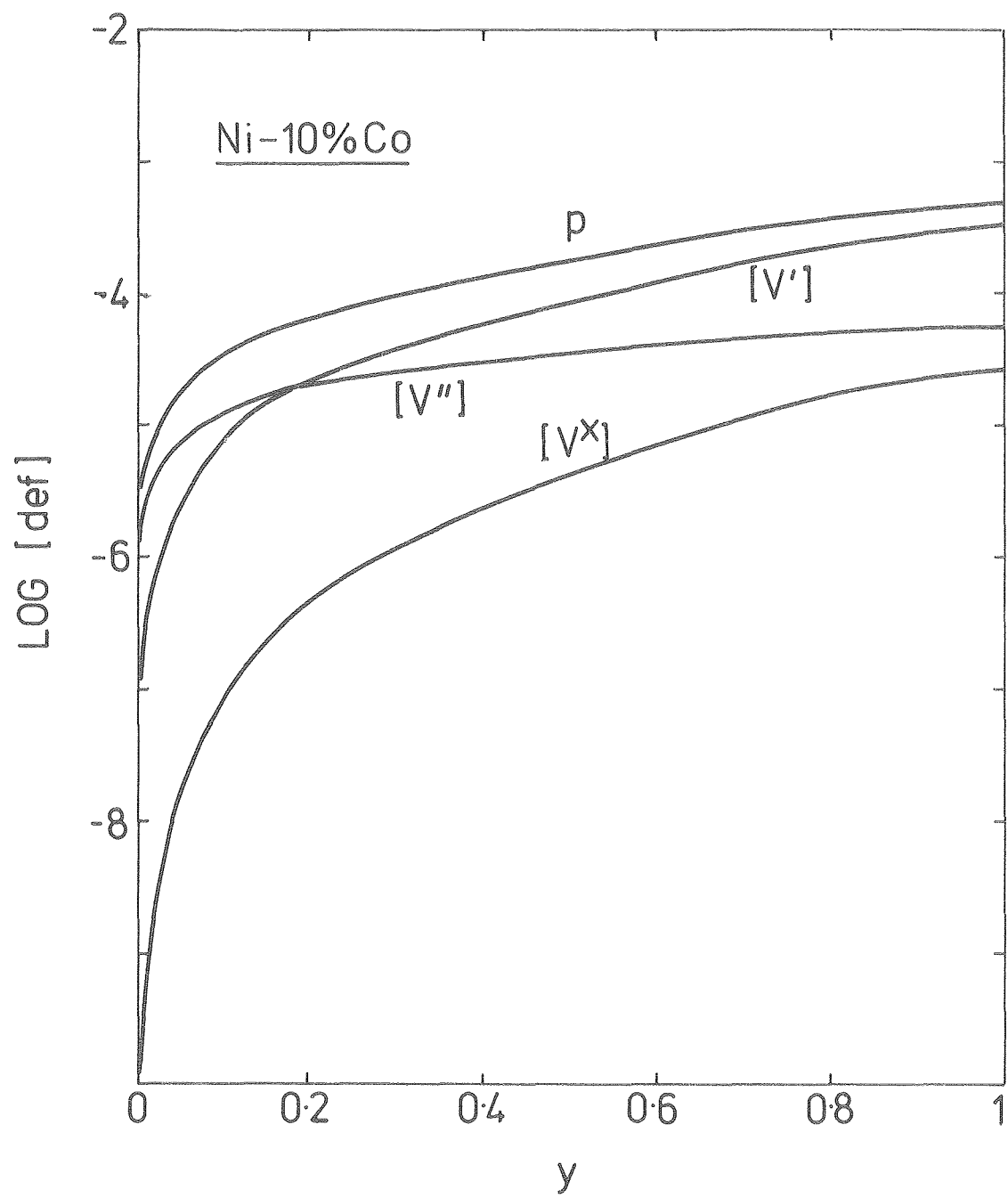
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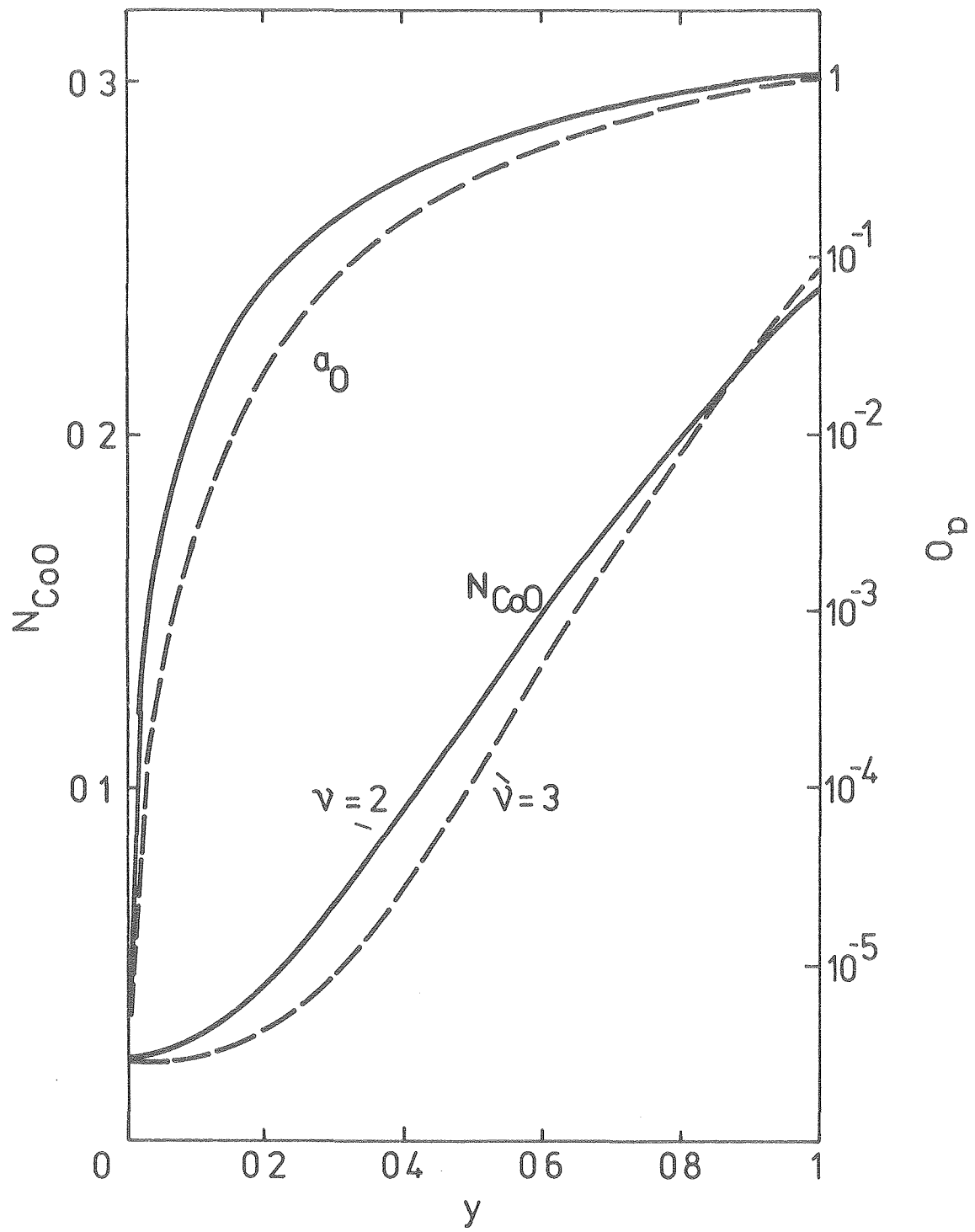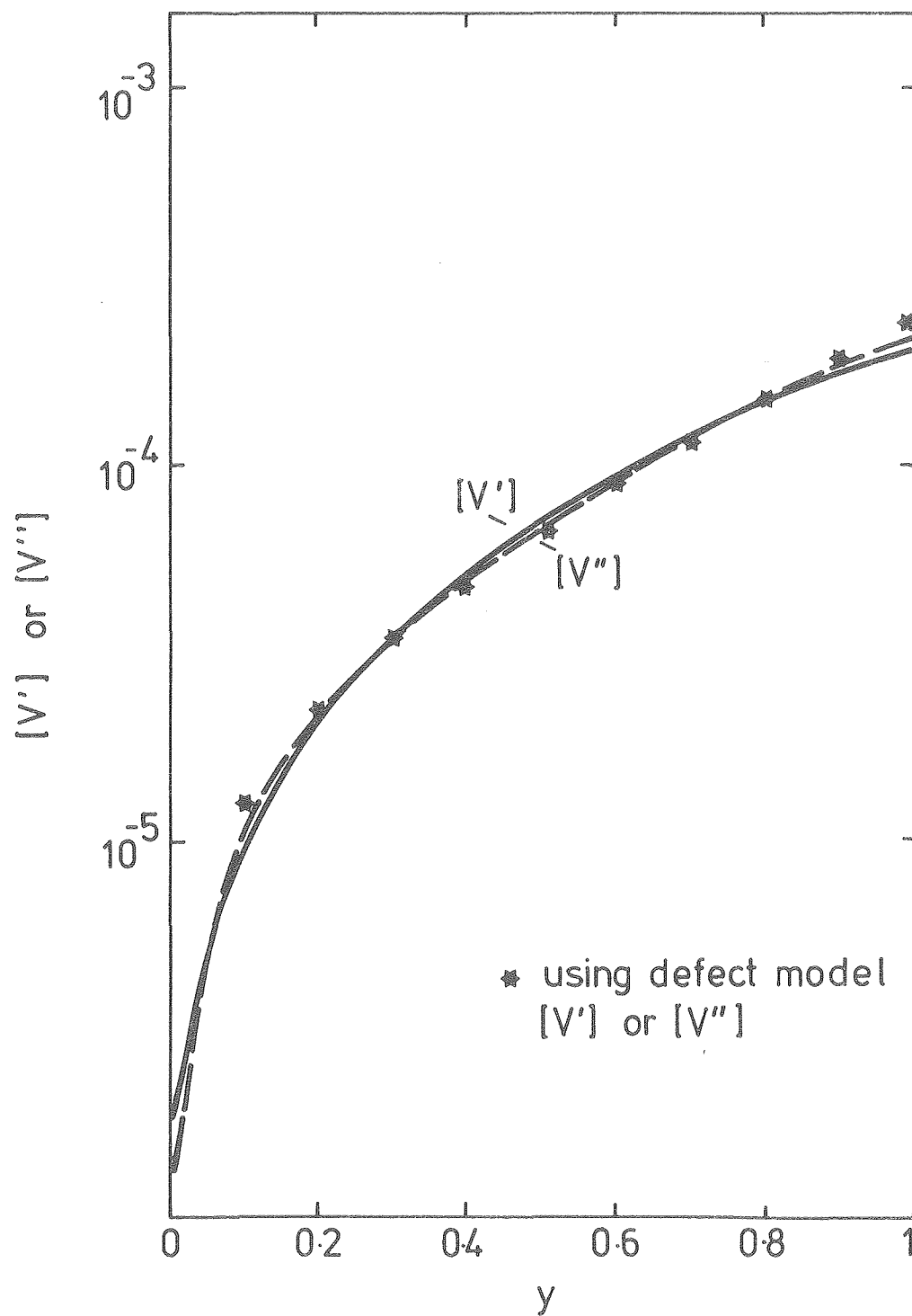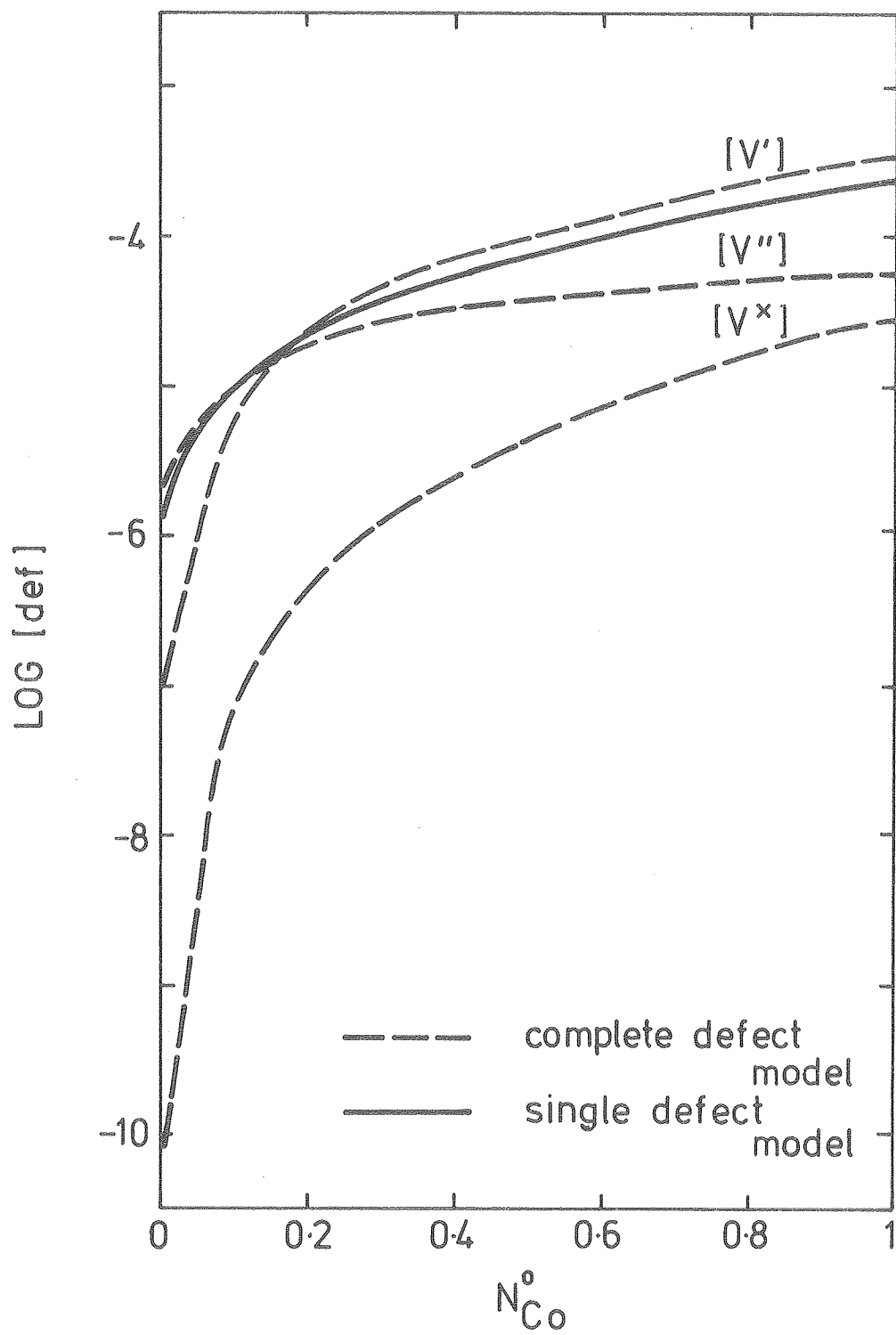Figure 2b

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Figure 2c

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Figure 2d

Figure 3

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Figure 4

Figure 5

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Figure 6